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STUDY OF ELECTROLYTIC DISSOCIATION IN STRONG ELECTROLYTES BY RAMAN EFFECT

MISCELLANEOUS SUBSTANCES : PHOSPHORIC ACID, BICARBONATES AND PERCHLORIC ACID

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ABSTRACT. In this paper, a detailed study of electrolytic dissociation in phosphoric acid and phosphates, bicarbonates and perchloric acid is described. Raman spectra of solutions of phosphoric acid are quite similar to that of sulphuric acid and the lines attributed to various kinds of radicals, H_3PO_4, H_2PO_4, HPO_4 and PO_4. A study of these lines in solutions of the acid and of the salt revealed that the dissociation of phosphoric acid is quite rapid as far as the removal of the first hydrogen ion is concerned, while further dissociation is very slow. No evidence for the dissociation of the ions is found in solutions of phosphates and bicarbonates could be traced from these studies. In solutions of perchloric acid, below 70%, evidence for the presence of undissociated molecules is found. It is concluded that this acid is not as strong as was supposed to be.

PHOSPHORIC ACID

Introduction.—Electrolytic dissociation in phosphoric acid and phosphates has been studied by a number of investigators including Nisi (1929), Bell and Jeppesen (1935), Schaefer, Matosi and Aderhold (1930), Hibben (1931), and C. S. Venkateswaran (1936). Nisi observed lines of frequencies 356, 498 and 911 for 84% acid, 512 and 906 for 50%, and 505 and 895 for 25% solutions of the acid. These results have been confirmed by Bell and Jeppesen. Nisi obtained lines at 358, 518, 889 and 1061 for a 38% solution of dihydrogen sodium phosphate and Schaefer and co-workers recorded a line at 924 for crystals of tertiary phosphate of ammonium. Venkateswaran worked with the acid in a number of concentrations. He also worked with solutions of a number of salts. The author attempted to study this acid also along with the substances published in this series (Rao, N. R., 1940, 1941, 1942) of investigations, and found that the results and conclusions of the previous authors require modification.

EXPERIMENTAL

The reason why comparatively little work is done in this acid by Raman effect is that its Raman spectrum is invariably found to be superposed by an intense spectrum. Somehow, it is found very difficult to remove this by purification of the acid. Therefore, other methods of diminishing this, *i.e.*, by making use of filters is resorted to.

First, the acid in the concentrated state is mixed with a little nitric acid—as in the case of sulphuric acid (Rao, N. R. 1940)—and heated up to 200°C, when most of the impurities would have oxidised. This is found to improve the spectrum to a large extent. Then the acid is filtered through a sintered glass funnel while hot. This removed the dust in the solution. Solutions of the salts are purified by treating them with purified carbon and then filtering through quantitative filter paper in a sintered glass funnel. Thus, solutions of the acid of concentrations, 75%, 50%, 30% and 15% of sodium dihydrogen phosphate of concentrations 5.7, 2.85, and 1.43N, of sodium monohydrogen phosphate of concentrations 2.5, and 1.5N and tertiary phosphate of concentration 1.0N are prepared.

Inspite of this laborious purification, continuous spectrum could not be avoided without the use of filters. Also, in the cases of dilute solutions of the acid and for the solutions of the salts, concentration being low, long exposures were required to get tolerably good spectra. In these cases, the continuous spectrum was suppressed to some extent, by using a double jacketted Wood's tube. The experimental liquid was placed in the innermost tube and two outer jackets were filled with solutions of sodium nitrite and of iodine in carbontetrachloride, in order to isolate the 4358 line of the mercury arc as much as possible.

RAMAN LINES OF PHOSPHORIC ACID AND PHOSPHATES

Of the work done by various authors, that of Venkateswaran (*loc. cit.*) is the most recent and in many respects exhaustive. Therefore, the Raman lines obtained by Venkateswaran are given here in Table I for the sake of convenience of comparison with those of the author given in table II.

TABLE I

Substance	Raman frequencies in cm^{-1}.						
H_3PO_4 85%	361(w.d),	495(w.d),	914(st),	--	.	.	.
60%	361(w.d),	495(w.d),	903(st),	—	-	--	—
30%	361(w.d),	405(w d),	890(v.st),	950(v.w)	—	1200(v.w)	—
15%	316(w d),	495(w.d),	886(v st),	959(w),	1082(w),	1194(w),	1427(w)
7.5%	316(w.d),	405(w.d),	886(st),	959(w),	1082(w),	1194(w),	1427(w)
3.0%	316(w d),	495(w.d),	886(st),	959(v.w)	1082(v.w)	—	—
NaH_2PO_4 27%	356(w),	495(v.w),	886(st),	—	1085(m).		
$(NH_4)_2HPO_4$ 30%	363(v.w),	515(v.w),	889(w),	975(st),	1070(w).		
$(NH_4)_3PO_4$ 31%	363(v.w),	515(v.w),		985(m),	1080(v.w).		
$(NH_4)_3PO_4$ crystal				951(w),	—		

TABLE II

Substance		Raman frequencies in cm^{-1}					
H_3PO_4	75%	360(w.d),	480(w.d),	914(st),	1060(v.w),	—	
	50%	360(w.d),	480(w.d),	903(st),	1060(v.w),	—	
	30%	390(w.d),	480(w.d),	890(st.b),	1060(v.w),	—	
	15%	360(w.d),	480(w.d),	886(st.b),	1060(v.w),	1200(v.w),	1450(v.w)
NaH_2PO_4	5.70N	360(m.d),	490(m.d),	886(st),	1060(st),	1200(v.w),	1450
	2.85N	380(m.d),	505(m.d),	886(st),	1070(st),	1200(v.w),	1450
	1.13N	380(m.d),	505(m.d),	886(st),	1080(st),	1200(v.w),	1450
Na_2HPO_4	2.50N	380(m.d),	515(m.d),	880(w),	990(st),	1080(v.w),	1450
	1.50N	385(m.d),	515(m.d),	880(w),	990(st),	1080(v.w),	1450
Na_3PO_4	1.90N	390(m.d),	515(m.d),	—	950(st),	1080(v.w),	1450

In the above tables, the letters in the brackets represent the intensities. w-weak; v. w-very weak; v. w. d-very weak and diffuse; w. d-weak and diffuse; m-medium; m. d-medium and diffuse; st-strong, st. b-strong and broad.

ASSIGNMENT OF RAMAN LINES TO DIFFERENT RADICALS

The Raman spectrum of phosphoric acid is quite similar to that of sulphuric acid and the assignment of lines to different radicals in the former can, therefore, be made on lines similar to that of the latter.

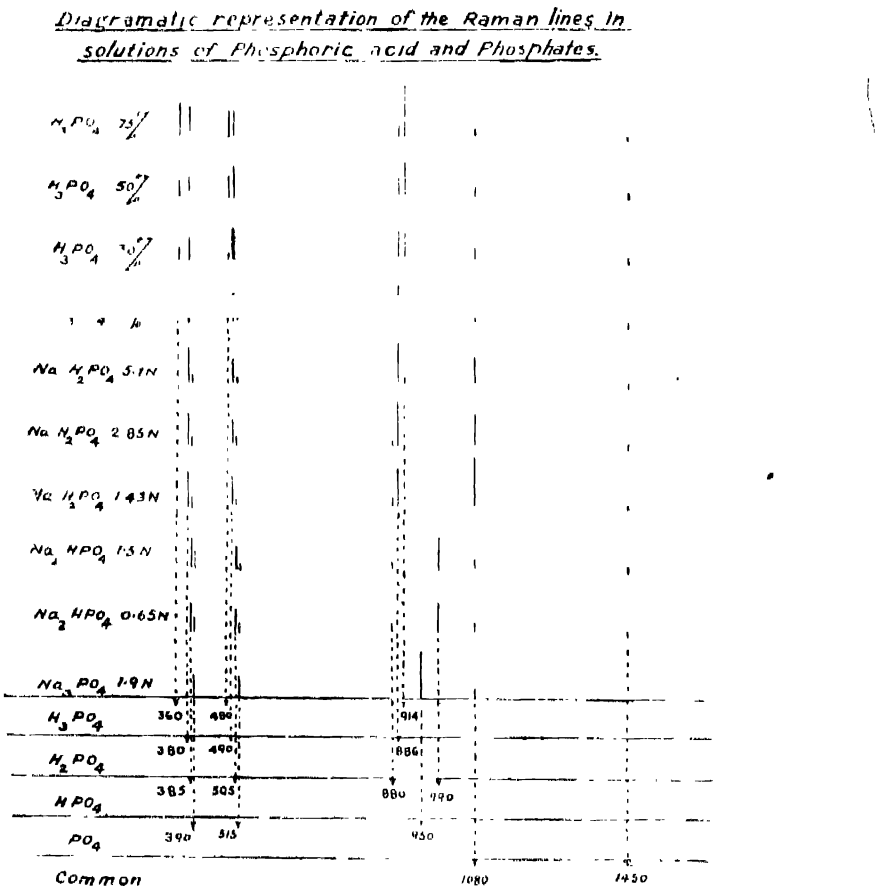
Venkateswaran assigned the lines at 1085, 980, 515, and 363 to PO_4, 1080, 975, 880, 515 and 363 to HPO_4, 1085, 885, 515 and 360 to H_2PO_4 ions. He did not assign any lines to H_3PO_4 molecules. He suggested that the line at 914 shifts to 880 as the acid is diluted from 85% to 3%. He seems to have regarded this as a concentration effect, and considered the acid to be largely dissociated into H_2PO_4 ions. This warrants a high conductivity for the acid even at high concentrations, while experiment shows that it is so even in comparatively weak acid.

Another point to be considered is that he gives 980 and 975 for the values of the lines characteristic of PO_4 and HPO_4 ions, while the corresponding lines in the spectra of the tertiary and secondary salts obtained by the author, are found to be well separated with a frequency difference of 40 cm^{-1}, the frequency difference in the spectrum of the secondary salt being greater than that of the tertiary, contrary to what is represented by Venkateswaran.

The groups of lines at 360, 515, 890 and can 1060 be regarded as composed of components corresponding to PO_4, HPO_4, H_2PO_4 and H_3PO_4, similar to those at 420, 550 and 900 in solutions of sulphuric acid, where they were considered to be composed of components corresponding to radicals SO_4, HSO_4 and

H_2SO_4. The line at 900 in sulphuric acid has a component at 860 corresponding to HSO_4 ions but with its specific intensity much less than its neighbour 910, characteristic of H_2SO_4. Similarly, for phosphoric acid, the line 890 appears to be very feeble and to have a little lower frequency in the spectrum of the secondary salt while in the the primary salt and acid, it is the most intense line.

On the above basis, the lines are assigned to different radicals and are represented in the diagram. The three groups of lines mentioned above are not resolved as represented in the diagram. Their resolution is exaggerated in order to make the assignment clear.



DIAGRAM

The line at 1080 which appears in all the spectra is of doubtful origin. It is most intense in the spectra of the primary salt. It is very diffuse in the most concentrated solutions and gets sharper with dilution. From its large intensity in the spectra of the primary salt solution, it is likely, that it is characteristic of the H_2PO_4 ions. Its appearance in the secondary and the tertiary salts may be due to the hydrolysis of these salts giving rise to the H_2PO_4 ions, which seem to the most stable of all the radicals mentioned above, both in the acid and salt solutions.

DISSOCIATION OF PHOSPHORIC ACID

The comparatively good intensity of the 886 line in the various spectra, it can be even in dilute solutions, indicates the predominence of H_2PO_4 ions even in very dilute solutions as was observed by Nisi, Venkateswaran and others. Also the absence of the 990 line in the spectra of the acid indicates that the further dissociation of H_2PO_4 into HPO_4 and H is very small even in dilute solutions of the acid. The behaviour of the acid in this respect is quite similar to that of sulphuric acid, and obviously due to similar reasons.

There is one important difference between sulphuric and phosphoric acids in this respect. While even in very concentrated solutions, ranging from about 15N, we find lines corresponding SO_4 ions, lines corresponding to HPO_4 or PO_4, are not found in the spectra with these concentrations of the acid. Venkateswaran, who worked with dilute solutions also, reported a weak line at about 950 corresponding to HPO_4 ions which he attributed to the further dissociation of HPO_4. Considering the fact that this line is very intense in the corresponding salts, it should be concluded that the number of HPO_4 ions in the acid solutions is very small.

The rapid shifting of the line 914 to 886 as the concentration is reduced from 75% to 15%, shows that the dissociation of the acid is quite rapid. But the conductivity data shows that the degree of dissociation is only 18% even in 16% acid. Since the calculation of the dissociation made in the later case involves many unfulfilled assumptions, which are well known, the value given for the degree of dissociation should be taken with some reserve. The acid is fairly strong as far as the removal of the first hydrogen ion is concerned.

DISSOCIATION OF PHOSPHATES

In solutions of NaH_2PO_4, the line at 1080 gets sharp and intense on dilution, but the line due to HPO_4 at 990 does not appear at all, thereby showing that the dissociation of H_2PO_4 into HPO_4 and H is very slow even in these concentrations, contrary to the dissociation of HSO_4 into SO_4 and H in solutions of acid sulphates.

The spectrum of Na_2HPO_4 does not change with dilution, and there are no lines in this spectrum corresponding to PO_4 ions, thereby showing that the dissociation of HPO_4 into PO_4 is also very slow.

DISSOCIATION OF BICARBONATES

Raman spectra of bicarbonates have been studied only by a few investigators, namely Dickinson and Dillon (1929) and I. R. Rao and C. R. Rao (1936). Dickinson and Dillon worked with a 26% solution of $KHCO_3$ and reported a line of frequency 1035. I. R. Rao and C. S. Rao referred to bicarbonates also in their note on "Electrolytic dissociation in strong electrolytes" and reported that the bicarbonates dissociate completely as far as the alkali radical is concerned and the acid radical dissociates progressively on dilution. A study of dissociation of bicarbonates with dilution will be described in the following.

EXPERIMENTAL

Raman spectra of these substances are found to be superposed by an intense continuous spectrum, which is found difficult to avoid even after laborious purification of the solutions. Therefore, two filters, a solution of quinine sulphate in dilute HCl and of iodine in carbon tetrachloride, are used. Since, quinine sulphate had to be replaced very often, the usual arrangement employing double jacketted Wood's tube could not be used. Light from a mercury arc is condensed by a condenser on to the Woods tube. Filters containing in rectangular glass cells are placed near the Wood's tube Long exposures of nearly 50 hrs. were required to get tolerably good spectra. Another difficulty experienced in this connection is that though clear solutions are prepared, after some time, they are found to attack the glass container a little and become slightly turbid. Since, this happens only after a long time, it is not very serious. Solutions of sodium carbonate (3.06N) and potassium bicarbonate (2.35N, 1.18N, 0.59N) are prepared with pure substances and treated as usual with carbon and filtered through a sintered glass funnel. The Raman spectra are photographed for times inversely proportional to the concentration.

RESULTS AND DISCUSSION

Only a few lines could be recorded with some intensity and the frequencies measured and are given in table III.

TABLE III

Substance	Raman frequencies in cm^{-1}.		
Na_2CO_3 3.06N		1060 (st)	—
$KHCO_3$ 2.35N	1040 (st)	1060 (v.w)	1400 (st)
1.18N	1040 (st)	1060 (v.w)	1400 (st)
0.59N	1040 (st)	1060 (v.w)	1400 (st)

It is quite probable that there may be many other weak lines of lower frequencies, but they could not be recorded. Raman spectra of carbonates both in crystals and solutions are taken by a number of investigators (Kohlrausch, 1931*a*). The crystals give rise to a number of sharp lines, while in solutions only one line could be recorded. Its frequency slightly varies from substance to substance also.

It can be seen from the Table III that the 1060 line is common to both solutions, carbonate and bicarbonate and can be taken to be characteristic of the CO_3 group. Lines of frequencies 1040 and 1400 are taken to be characteristic of HCO_3 ions. Now, for CO_2 there is a Raman line at 1408 (Kohlrausch, 1931*b*). From this it can be concluded that the HCO_3 ion has a structure $CO_2.OH$, where H is attached to O, as in the case of all the other acids. The 1040 line seems to correspond to the 1010 line of acetic acid attributed to C-O bond.

The spectra of the bicarbonate solutions show little changes in the intensities of the lines with dilution, thereby showing that the dissociation in these solutions vary very little with dilution, as in the case of phosphates. Now, carbonic acid H_2CO_3 is known to be very weak and hence in solution of sodium carbonate, hydrolysis can be expected to take place resulting in the production of HCO_3 ions. The absence of lines due to HCO_3 in the carbonate solution indicates that this process is also very slow.

PERCHLORIC ACID

Perchloric acid is well known to be a very strong acid. Investigators (Kohlrausch, 1931c) in this field found that even a 70% acid gives the same Raman lines as the solution of the corresponding salt, unlike in the case of nitric acid and other acids which show two sets of lines attributable to the undissociated molecules and their ions. This suggests that this acid is completely dissociated in solutions below 70%. The present work is intended to test this point.

Perchloric acid has been successfully studied by Fontoyne (1936) at different concentrations. For pure acid, he observed lines of frequencies 452(1), 570(5), 730(5), 922(0), 1025(4), and 1190(0), corresponding to $HClO_4$ molecules and for $NaClO_4$ at 463(1), 626(1), 935(8), and 1110(0), corresponding to ClO_4 ions. It can be seen that these spectra are quite similar to those of H_2SO_4 and its ions. Table IV gives the lines and their intensities in these solutions as studied by the author.

TABLE IV

Solution	Raman frequencies in cm^{-1}			
$HClO_4$ 10N	450(1)	610(1)	930(5)	1120(0)
$NaClO_4$ 10N	463(1)	626(1)	935(8)	1110(1)
$HClO_4$ 7·5N	455(1)	610(1)	930(6½)	1120(0)
$NaClO_4$ 7·5N	462(1)	462(1)	935(8)	1110(0)
$HClO_4$ 5·0N	455(1)	610(1)	930(7½)	1120(0)
$NaClO_4$ 5·0N	462(1)	626(1)	935(8)	1110(0)

The above spectra are taken under identical conditions with times of exposure inversely proportional to concentration. From the above table the following points can be clearly seen.

1. At the outset, it appears that the Raman spectra of the acid and the salt consist of the same lines, that is those characteristic of only the acid radical, and the lines due to undissociated acid molecules could not be observed in these solutions.

2. The lines of frequencies 463 and 626 slightly shift to shorter frequencies in the spectra of the acid compared to that in the salt.

3. The intensity of the line at 935 characteristic of the ions becomes larger with increasing dilution of the acid, while that in the salt solution is the same in all concentrations.

4. For each concentration, the intensity of this line is larger in the spectrum of the salt than in that of the acid.

DISCUSSION

The results 2-4 are not to be expected if the acid is completely dissociated. (2) indicates the presence of the lower frequency components due to the undissociated molecules. From 3 and 4, it is evident that the acid is not completely dissociated in these solutions, as was thought by the previous investigators. The absence of the lines due to the undissociated molecules simply means that the specific intensity of the lines due to these molecules is very small compared to those due to the ions. This view is further supported by the fact, that in the case of sulphuric and nitric acids also, where a quantitative investigation of the dissociations are reported by the author, it was found that the lines corresponding to the undissociated molecules have less specific intensity than those of the ions.

In conclusion, the author takes great pleasure in recording his grateful thanks to Dr. T. Ramakrishna Rao, D.Sc. (Lond.), under whose direction the present work was done.

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